A STUDY OF FILMS ISOLATED FROM PASSIVE STAINLESS STEELS[1]

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ABSTRACT

By use of a bromine-methanol solution the authors have been able to isolate passive films from electrolytic chromium, ferritic, and austenitic stainless steel, and from the alloys "Nichrome" V and "Inconel." The films were very thin and transparent and were found to be formed on initially film-free (pickled) surfaces by air exposure and by passivation treatments in HNO_3 and in HNO_3-$K_2Cr_2O_7$ solutions.

These passive films have been examined by both light microscopy and electron microscopy and by electron diffraction. Chemical analyses indicate that both chromium and iron are major constituents in the films from Type 430 and Type 317 stainless steel. It is believed that these are present together in solid solution, possibly in a spinel type of crystalline lattice.

The films from chromium passivated in HNO_3 have been shown to contain a high percentage of chromium, probably as Cr_2O_3.

INTRODUCTION

The corrosion resistance of stainless steels and related alloys has long been attributed to the presence of invisible surface oxide films, continuous in nature and of unknown structure and composition. Because no direct experimental evidence has ever been presented to substantiate the presence of such films, numerous other theories to explain passivity have been postulated. One such theory that ascribes no primary importance to surface oxide films but attempts to explain passivity on the basis of electron sharing has been advanced recently by Uhlig and Wulff (1). This "electron configuration" theory has aroused much interest and has stimulated considerable research and critical discussion.

In a previous paper (2) initial work on the passivity behavior of stainless steels was described, and it was shown that different degrees of passivity could be conferred on these alloys by varying the passivating medium and the conditions of passivation, i.e., time, temperature, etc. The data obtained from those investigations pointed to the presence of strong, invisible "passive" films as being responsible for the observed corrosion behavior of the materials tested. No direct evidence of the presence of passive films could be cited, however.

The present work is presented as a continuation of the earlier studies and does offer direct evidence that the passivity of stainless steel results from surface oxide film formation. This paper describes the isolation of

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films from passive stainless steel and initial investigations conducted upon their physical and chemical nature. The results reported here are in a sense largely incomplete, but it is believed that the present work represents the first time that oxide films have been isolated from stainless steel specimens known to be passive as a result of air exposure or low-temperature passivation treatments. It is hoped that the techniques and results given here will stimulate other research on this subject to clarify further the mechanisms of passive film formation and of passivity phenomena produced.

EXPERIMENTAL WORK

Specimens and their preparation

In the present study of passive films, three types of stainless steel—15-16 Cr (AISI type 430), 18-8-S (AISI type 304), and 18-8-Mo (AISI type 317)—and electroplated chromium were investigated. Some preliminary work has also been done on the alloys "Inconel" and "Nichrome" V. The chemical composition of all these materials is listed in Table I.

TABLE I.—*Composition of alloys used in passive-film studies*

Material	C	Cr	Ni	Mn	S	P	Si	Mo	Fe
AISI Type 430 Stainless Steel	0.10	15.55	0.314	0.39	0.017	0.018	0.39	—	bal.
AISI Type 304 Stainless Steel	0.069	18.65	8.92	0.52	0.018	0.020	0.30	—	bal.
AISI Type 317 Stainless Steel	0.06	18.24	14.08	1.70	0.018	0.018	0.46	3.06	bal.
"Nichrome" V		20.00	80.00*						
"Inconel"	0.08	14.0	78.5	0.25	0.015	—	0.015	—	6.5

*Nominal Composition.

All specimens were finished on a 120X emery belt and then given a bright pickle with a HNO_3-HF-HCl solution (composition: 120 ml. of 65% HNO_3, 20 ml. of 48% HF, and 10 ml. of 37% HCl per liter of solution). In pickling Type 430 stainless (a ferritic alloy) and "Nichrome" V, a pickling smut was formed that had to be brushed off. The other alloys all pickled bright and clean by warm (60–80°C.) pickling solution which dissolved all surface oxide film formed by the previous grinding operation. The specimens were then washed in distilled water and either air-dried (this constitutes "air-passivation") or given an immersion passivation in 30% HNO_3 or in a solution of 5% HNO_3 containing 0.5% $K_2Cr_2O_7$. The time and temperature of the passivation treatments were varied over wide ranges.

Specimens of chromium were prepared by electroplating the metal onto one face of a thin sheet cathode of 90 Cu-10 Zn alloy. A standard plating solution of 250 g./L CrO_3 and 2.5 g./L H_2SO_4 was used at a current density of about 2 amp./sq. in. (0.129 amp./dm.^{2}) to form a chromium plate several thousandths of an inch in thickness. The copper alloy backing strip was then dissolved away with strong HNO_3, leaving fragments of thin sheets of passivated pure chromium. In one case small flakes of chromium were mechanically stripped from the backing metal to avoid

exposure to nitric acid. The specimens so obtained were assumed to be air-passivated.

"Sulfuric acid passivity"[2] for the alloys 15-16 Cr, 18-8-S, and 18-8-Mo was also investigated in this study. When stainless steel is actively corroded in sulfuric acid, then washed and exposed to air, it becomes passive and remains so for extended indefinite periods upon reimmersion in the same or higher concentrations of sulfuric acid. In these studies specimens were finished on a 120X emery belt, corroded in boiling 3–10% H_2SO_4, washed, air-dried, and reimmersed in 10% or higher sulfuric acid to determine if the specimens had become passive.

Mechanism of film stripping

The studies that resulted in the actual isolation of films from passive stainless steels were preceded by studies of bulk surface oxides produced by high-temperature oxidation. The results of this work, although highly informative, will not be reported here but will be the subject of a paper to be presented at a later date. These heavy films were stripped with a solution of iodine in anhydrous methanol. This reagent was used by Vernon, Wormwell, and Nurse, who have studied oxide films both on iron (3) and on polished 18-8 stainless steel (4). Iodine in methanol solution attacks the oxide-metal interface, freeing the film and allowing it to float in the solution. Although this reagent was satisfactory for stripping these less protective bulk oxides, it was not sufficiently aggressive to remove thin passive films in the times employed by the authors. However, it was found that bromine in methanol solution works similarly and that bromine is sufficiently more corrosive than iodine that stripping times for bulk films are greatly reduced. In addition, specimens from which film previously could not be stripped were stripped with no special difficulty using the bromine reagent. Stripping operations were carried out at room temperature in shallow glass-covered dishes filled with bromine-methanol solution. The concentration most generally used in these experiments was 10 ml. of bromine per 100 ml. of methanol, but the concentration is not critical. Both technical grade and anhydrous methanol were employed with equal success. The anhydrous solvent was prepared by refluxing the technical grade methanol over calcium oxide, distilling, and redistilling over calcium metal.

In the stripping technique, passivated specimens were scribed with a sharp tool to expose film-free stainless surfaces and were immediately immersed in the stripping solution. The concentration of corrosion along the scratch lines results in the undermining of the passive film in the manner shown schematically in Fig. 1. Films produced by the HNO_3-$K_2Cr_2O_7$ treatment were the most difficult to remove and rather long stripping times, 24 hr. or more, were necessary to isolate pieces of film of a size convenient to handle and to collect. Films on 18-8-S stainless steel passivated in 30% HNO_3 or merely by air exposure were stripped more easily, indicating that the oxide films so formed were not so protective. This confirms previously reported work (2). Passivated 15-16 Cr samples were stripped

[2] "Sulfuric acid passivity" is a misnomer in that the passive film is formed by air-passivation, after pickling in sulfuric acid.

most readily, a few hours being sufficient to undermine completely the film on a sample 1 in. wide x 2 in. long. (2.5 cm. x 5.1 cm.)

Samples of isolated film were collected by fishing them out of the bromine solution with a piece of 200-mesh (0.074 mm. hole) stainless wire screening. Washing of the film was accomplished by transfer through several successive dishes of fresh methanol.

Examination of Passive Films

In order to study the nature of the films isolated from passive surfaces, the authors have photographed them, employing both the light microscope to obtain photomicrographs of fragments caught on glass microscope slides, and an RCA type EMU electron microscope to obtain electron micrographs of specimens caught on 200-mesh (0.074 mm. hole) wire screens.

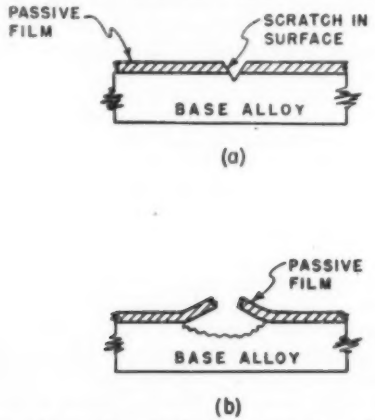

FIG. 1. Action of bromine-methanol solution on passivated stainless steel. (a) Cross-section of scribed, passivated surface. (b) Same cross-section after short exposure to solution.

These latter samples also served as specimens for transmission electron diffraction studies. Because of their fragility the films did not remain unbroken but tended to collapse as they dried on the supporting screen. Reflection electron diffraction patterns showing evidence of the passive film have been obtained from passive metal surfaces. Spectrographic analyses consisting of simply burning a sample of film in the carbon arc of a Bausch & Lomb Littrow spectrograph were carried out. The lines of the elements present were identified and a visual attempt was made to rate the elements present as major, minor, or trace elements.

Chemical analyses have been carried out by the W. B. Coleman Co., in Philadelphia. Samples of film weighing a few milligrams or less were collected by mass stripping experiments and analyzed by colorimetric techniques employing a Coleman No. 11 Universal spectrophotometer. Actual analytical procedures are described in detail in Appendix A. In this paper all analytical data have been converted to percentage of oxide.

The chemical analyses reported in this paper are subject to several possible sources of error that have not yet been investigated. SiO_2 is reported as high in all instances and its concentration increases with increased stripping time. Two possible sources of error exist: SiO_2 contamination may have come from the glass apparatus in which all stripping and many analytical procedures were carried out, or it may have resulted from the corrosion of the base metal during the stripping procedure itself. SiO_2 is not soluble in the stripping reagent and any silicate inclusions in the base metal would be present in proportion to the extent of the base metal corroded in stripping. With these facts in mind, all chemical analysis data are reported both as-received and on a SiO_2-free basis. Calculated on a SiO_2-free basis, the analytical data appear quite reasonable.

Because of difficulties in stripping the oxide film from known areas of samples, and in obtaining enough film to weigh accurately, the present work does not attempt to measure the thickness of the films isolated from stainless steel.

RESULTS AND DISCUSSION

Passive films from 18-8-S (AISI type 304) stainless steel

Very thin transparent films, presumably oxide in nature, have been isolated from 18-8-S passivated by air, by HNO_3, and by $HNO_3 + K_2Cr_2O_7$. Similarly appearing film (Fig. 2a) has also been isolated from "sulfuric-acid-passivated" specimens. Fig. 2b is a photomicrograph at 150 diameters of film from a HNO_3-$K_2Cr_2O_7$ 18-8-S specimen. The photograph shows what appears to be a reproduction of grain boundaries in the base metal, although similarly appearing lines are present which represent creases formed in the film as it dried upon the glass surface. Fig. 2c is an electron micrograph at 10,000 diameters of similar oxide film. Contamination of the film by particles of some sort is evident in this picture. An electron diffraction pattern of the same film (Fig. 2d) gives some evidence of crystallinity, but the rings are diffuse and difficult to measure accurately. As is usually the case with diffraction patterns, considerable definition has been lost in reproduction. Table II lists the interplanar spacing values as determined by electron diffraction studies of this type of film and also of the other passive films and passivated specimens covered in this study. The diffraction investigations are discussed in a later section.

Investigation of these types of stainless steel has led to the conclusion that passive films are definitely oxide reaction products of the metal and the passivating medium. Prolonged exposure of stainless steel in HNO_3 or HNO_3 containing $K_2Cr_2O_7$ at room temperature or boiling temperature resulted in the formation of oxide films of sufficient thickness to show interference tints. Specimens immersed for two months in a HNO_3-$K_2Cr_2O_7$ solution became covered with oxide films ranging in color through second-order green. Such thicker oxide films show clearly how grain boundaries are reproduced in the oxides. Fig. 3 is a photomicrograph of an oxide film thick enough to show a first-order blue color. Where the stripped film has doubled its thickness by folding back onto itself, a great increase in the amount of reflected light was observed.

The most important fact, however, that these tests have shown is that definite passivation conditions are necessary to build passive films of

optimum protective power and corrosion resistance. This confirms the break-through potential data, (2) which also indicated such an optimum protection. The films of necessity must be very thin, too thin to show interference tints. The curve in Fig. 4 gives average percentage weight losses (four specimens for each passivation time were tested) of 18-8-S stainless steel in 10% $FeCl_3 \cdot 6H_2O$ vs. time of passivation in boiling 5%

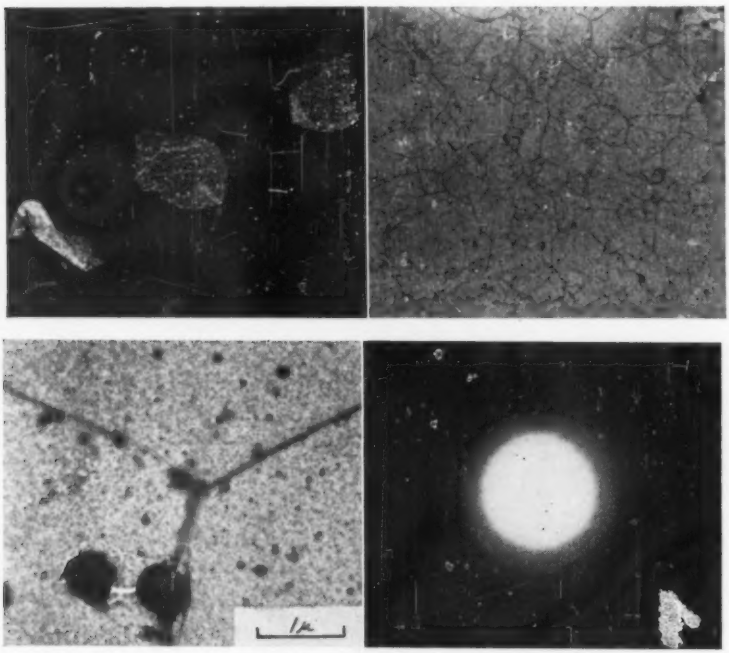

FIG. 2. Film from passive 18-8-S stainless steel. (a, Upper left). Photomacrograph of film fragments (from H_2SO_4-passivated specimen) on glass over black background. 6×. (b, Upper right). Photomicrograph of film from HNO_3-$K_2Cr_2O_7$-passivated specimen. 150×. (c, Lower left). Electron micrograph of film (b). 10,000×. (d, lower right). Transmission electron diffraction pattern of film (b).

HNO_3 + 0.5% $K_2Cr_2O_7$. The minimum in the curve indicates the optimum time of passivation.

Surface oxide films have been isolated for all these passivation conditions. In the case of freshly pickled specimens given a minimum of air exposure, the surface of stainless steel is immediately uniformly attacked by the stripping solution. Scratch lines in the surface of such specimens do not show any preferential attack, indicating that no stable film has yet formed.

From the investigation of "sulfuric acid passivity" of 18-8-S, the authors are convinced that the passivity produced by air or oxygen exposure subsequent to H_2SO_4 corrosion is also the result of oxide film formation. Films

have been stripped from surfaces so passivated, and air or oxygen exposure is necessary to produce passivity by this method. Tests of 18-8-S stain-

TABLE II.—*Results of electron diffraction studies**

Material	Specimen treatment	Interplanar spacings (Angstroms)	Remarks
Passive film from 18-8-S stainless steel (type 304)	Metal pickled, then passivated in 5% HNO_3-0.5% $K_2Cr_2O_7$ 30 min. at 60°C.	[2.48-2.53]* [2.05-2.08] [1.44-1.47] 1.16-1.18	Diffuse pattern, difficult to measure accurately
Passive film from 18-8-S-Mo stainless steel (type 317)	Similar passivation	[2.56] [2.09] [1.465] 1.19 1.04 0.920 0.840	Diffuse pattern again, but more measurable rings
Passive film from 15-16 Cr stainless steel (type 430)	Similar passivation	4.65 [2.53] [2.06] [1.45] 1.18 1.10 1.03	Diffuse rings
Passive film from electrolytic chromium	Chromium was exposed to 30% HNO_3	2.57 2.08 1.49	Very diffuse rings only three measurable
Oxide film from 18-8-S stainless steel (type 304)	Metal pickled, then heat-tinted 90 sec. in molten $NaNO_3 - KNO_3$ to yellow interference color	2.99 1.197 [2.48] 1.104 [2.08] 1.05 1.71 0.961 1.62 0.928 [1.48] 0.855 1.275 0.806	Sharp rings, pattern is that of Fe_3O_4
Oxide film from 18-8-S stainless steel (type 304)	Metal pickled, then boiled in conc. HNO_3. Blue interference color formed	4.70 [2.55] [2.08] [1.48]	Very diffuse lines fit cubic spinel Fe_3O_4 lattice
Reflection diffraction of 18-8-S stainless steel (type 304)	Specimen polished, electrolytically etched in oxalic acid, passivated in 5% HNO_3 + 0.5% $K_2Cr_2O_7$ at 60°C. for 60 min.	2.53 2.12 1.80 1.80 1.635 1.48 1.30	Lines at 2.53Å. and 1.48Å. are diffuse. Others fit face-centered cubic lattice of austenite

* Brackets indicate the most intense rings.

less were run in boiling H_2SO_4 of various concentrations under controlled atmospheres of air, oxygen, and nitrogen. After a period of corrosion, specimens were raised out of the acid and suspended in the atmospheres listed above. The stainless specimens suspended in air or oxygen for

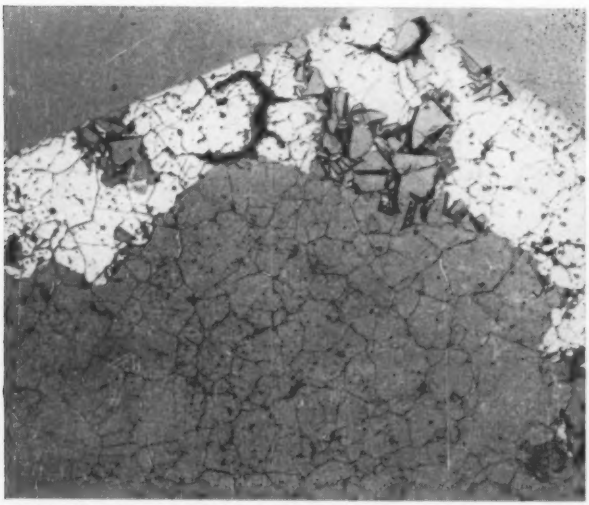

FIG. 3. Oxide film from 18-8-S stainless steel colored to first-order blue interference tint by HNO_3-$K_2Cr_2O_7$ solution treatment. 100×.

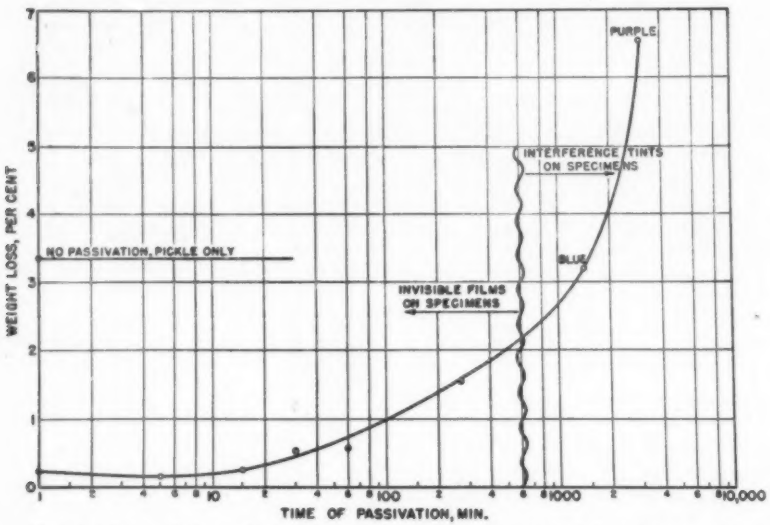

FIG. 4. Effect of time of passivation on weight losses of 18-8-S stainless steel in ferric chloride. Passivation treatment: 5% HNO_3-0.5% $K_2Cr_2O_7$, boiling. Test conditions: 10% $FeCl_3 \cdot 6H_2O$, 144 hr., room temperature.

short periods (1 hr. or less) were passive to further corrosion in the same acid. Specimens similarly exposed in the nitrogen atmosphere even for

24 hr. always remained active and would corrode vigorously when reimmersed in the sulfuric acid.

Passive films from 18-8-S-Mo (type 317) stainless steel

The same type of thin, transparent films has successfully been isolated from type 316 (18-8-S-Mo) stainless steel. The films were stripped cleanly with little contamination evident. Fig. 5a is a photomacrograph of small

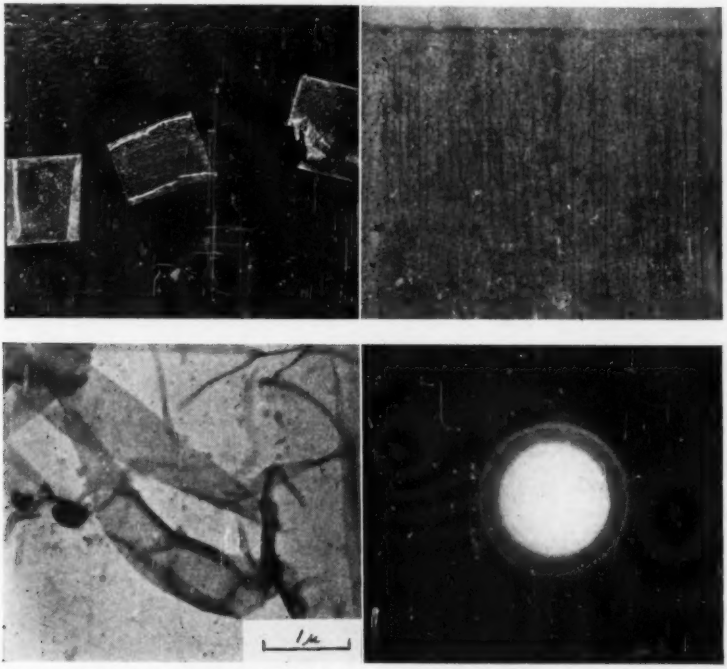

FIG. 5. Film from passive 18-8-S-Mo stainless steel (passivation by HNO_3-$K_2Cr_2O_7$). (a, Upper left). Photomacrograph of film on glass over black background. 6×. (b, Upper right). Photomicrograph of film. 100×. (c, Lower left). Electron micrograph of film. 10,000×. (d, Lower right). Transmission electron diffraction pattern of film.

squares of film stripped from specimens passivated in 5% HNO_3 − 0.5% $K_2Cr_2O_7$ for 30 min. at 60°C. Fig. 5b is a photomicrograph of the same film, and Fig. 5c, an electron micrograph. Folds in the film are evident and it has little "fine structure" of its own. Transmission electron diffraction of the film gave the same diffuse ring pattern (Fig. 5d) that was obtained for film from 18-8-S stainless steel.

The spectrographic plate obtained for a very small sample of such film has not been interpreted with certainty. Silicon appeared to have the most dense lines. Iron and chromium were reported as trace elements.

The chemical analysis was reported as:

		Calculated on SiO_2-free basis
	%	%
Fe_2O_3	23.08	53.6
CrO_2	13.84	32.1
NiO	0.0	
MoO_3	5.38	12.5
SiO_2	56.92	

Passive films from 15-16 Cr (type 430) stainless steel

Squares of film of a size corresponding to the scribed cross-hatching of the specimen surface were obtained with no difficulty from 15-16 Cr stainless steel. The film was grayish in color and more easily visible. Fig. 6a is a low-magnification photograph of the film on a glass slide. Fig. 6b and 6c are at higher magnifications. Fig. 6c shows that the base passive film, which is extremely thin, is covered with clusters of rod-shaped crystals. These are also evident in the electron micrograph of Fig. 6d. The lack of structure in the base film is seen very clearly here. The composition of the contaminating crystals has not been determined. Stripping of the 15-16 Cr is accompanied by the production of much grayish-black powder, which probably consists of carbides. It does not seem likely that the crystals could be iron or chromium bromides, since the latter are readily soluble in alcohol.

Electron diffraction examination (Fig. 6e) again revealed the same type of pattern with the same interplanar spacings, within the accuracy of measurement, that were obtained for the films from Types 304 and 317 stainless.

Spectrographic analysis reported chromium and iron as the major elements in the film. The chemical composition of the film was reported as:

		Calculated on SiO_2-free basis
	%	%
Fe_2O_3	23.10	23.7
Cr_2O_3	70.0	71.7
SiO_2	2.38	

Passive film from chromium

Subsequent to the studies conducted on the stainless steels, the same techniques were employed on thin sheets of electrolytic chromium. The bromine-methanol method proved eminently successful again. Chromium dissolved away rapidly leaving a "shell" consisting of the original passive oxide film, on the metal. Dilute bromine solutions were employed. The same type of film was obtained both from HNO_3-passivated chromium (as was produced by HNO_3 solution of the copper alloy backing sheet) and from air-exposed chromium. The film was quickly and easily collected. Large pieces had a "glassy" appearance and showed any striations or markings originally present on the copper alloy cathode reproduced in

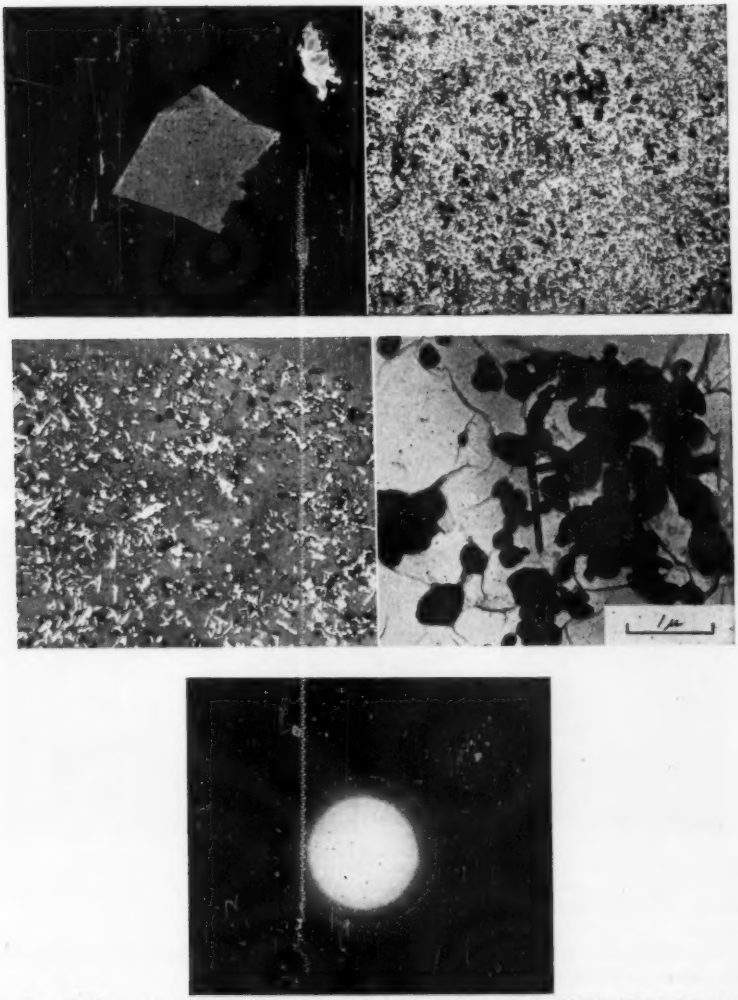

FIG. 6. Film from 15-16 Cr stainless steel (passivation by HNO_3-$K_2Cr_2O_7$). (a, upper left). Photomacrograph of film on glass. 6×. (b, upper right). Photomicrograph of film. 100×. (c, center left). Same as (b). 750×. (d, center right). Electron micrograph of film. 10,000×. (e, lower center). Transmission electron diffraction pattern of film.

negative on the underside of the electroplated chromium. When collected in aggregate form and viewed against a white background, the color of the film was light green, an indication that it could be chiefly chromium

oxide. This observation was checked both by the spectrographic plate, which showed chromium having very strong lines, and by actual chemical analysis of the film. The film was analyzed as containing 76.66% Cr_2O_3. Also reported were 2% CuO, 12% Fe_2O_3, and 6% SiO_2. On a silica-free basis the figures would be 81.6% Cr_2O_3, 12.8% Fe_2O_3, and 2.1% CuO.

Fig. 7a and 7b are photographs of the film from chromium. Fig. 7c is an electron micrograph. The latter micrograph shows that the film is

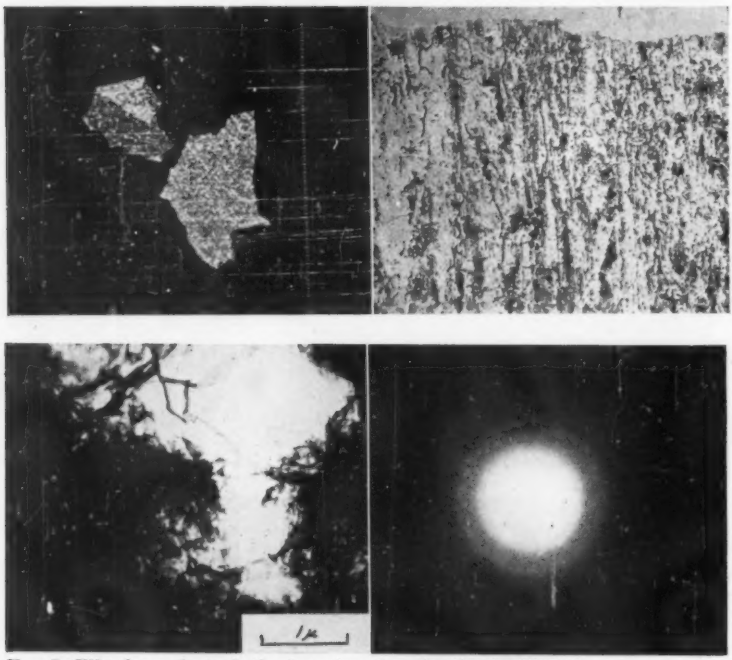

FIG. 7. Film from electrolytic chromium (passivation by HNO_3). (a, upper left). Photomacrograph of film on glass. 6×. (b, upper right). Photomicrograph of film. 500×. (c, lower left). Electron micrograph of film. 10,000×. (d, lower right). Transmission electron diffraction pattern of film.

relatively thick. (Actually it is present in double thickness, since originally it covered both sides of the thin chromium sheet.)

It may be noted here that the electron diffraction pattern (Fig. 7d) is again the same one that was obtained for films isolated from the stainless steels. The interpretation of the diffraction patterns is discussed below.

"Nichrome" V and "Inconel"

These alloys combine good corrosion resistance with refractory qualities. Both are high-nickel alloys containing, respectively, 20% and 14% of chromium. Stripping experiments with these alloys exposed to air after

pickling or passivated in HNO_3 or HNO_3-$K_2Cr_2O_7$ solutions were also successful in isolating very thin surface oxide films. Again it was noted by the corrosive action of the bromine-methanol that the air-exposed specimens had least corrosion resistance to the reagent and that the film formed by the HNO_3-$K_2Cr_2O_7$ treatment was most protective and adherent to the base metal.

No other work has been done in studying passive films isolated from these alloys. Further work should undoubtedly be undertaken to determine the physical and chemical nature of the films.

Discussion of electron diffraction studies

According to the interplanar spacings data of Table II, it appears that all the passive films investigated have a similar type of crystalline or semi-crystalline lattice structure. The same three intense, diffuse lines were found in each pattern. Until the study made on film from chromium had been made, the other diffraction patterns were interpreted as belonging to a cubic spinel type of lattice, such as Fe_3O_4 occupies. According to x-ray diffraction data of Fe_3O_4, the strongest line is found at 2.53Å., the second strongest at 1.483Å. No intensity rating is given the line at 2.10Å. No attempt has been made visually or photoelectrically to rate the relative intensities of the three lines. It is well known that the line intensities in x-ray and electron diffraction patterns of the same substance are not always in direct agreement. As Table II indicates, the same three intense lines were found in the diffraction patterns of 18-8-S stainless steel exposed to nitric acid sufficiently long to form a blue interference color. The diffraction patterns of film formed by heat-tinting in molten nitrates also give these same three lines. In heavier films the lines are sharper and almost certainly result from diffraction by a cubic spinel (Fe_3O_4) lattice. The fact that films from chromium gave the same type of pattern can be reconciled only if we admit the formation on chromium of a spinel oxide of the type $Cr_2O_3 \cdot CrO$ (or Cr_3O_4). The other alternative is the possibility that the pattern is a diffuse one of Cr_2O_3. However, in this case the agreement with x-ray data is not good.

Even though the interpretation of the structure of passive films from stainless steel and chromium is uncertain, the diffuseness of the patterns is indicative of a finely crystalline state, one approaching an amorphous nature. A series of transmission diffraction patterns was made of samples stripped from 18-8-S stainless steel oxidized in molten nitrates for varying lengths of time. As time of oxidation decreased, the decrease in film thickness was accompanied by an increase in the diffuseness of the diffraction patterns. Fig. 8a and 8b illustrate this effect. The thinner film was very light yellow in color and probably of the order of 300–400Å. in thickness. Because of this the passive films on stainless steel may be considerably thicker than has commonly been conjectured in the past. Because of their failure to give sharply crystalline patterns, we cannot assume that the films are extraordinarily thin. Very likely this diffuseness of diffraction pattern rings is responsible for the failure of investigators in the past (1, 2) to report the definite presence of oxide films on passivated stainless steel examined by reflection electron diffraction methods. In the present study, evidence of oxide film on stainless has been obtained by reflection methods.

Both air-exposed and HNO_3-$K_2Cr_2O_7$-passivated austenitic 18-8 surfaces showed the diffuse band evidence of a thin film of oxide. Fig. 9 reproduces a reflection diffraction pattern of the surface of polished, etched, and passivated 18-8-S stainless steel. The diffuse bands indicative of oxide are

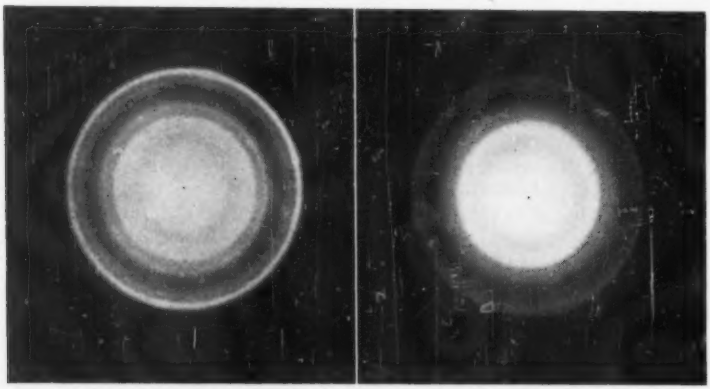

FIG. 8. Transmission electron diffraction patterns of oxide film from heat-tinted 18-8-S stainless steel. (a, left). Oxidation time 120 sec. in molten (370°C.) $NaNO_3$-KNO_3. (b, right). Oxidation time 10 sec. in molten (370°C.) $NaNO_3$-KNO_3.

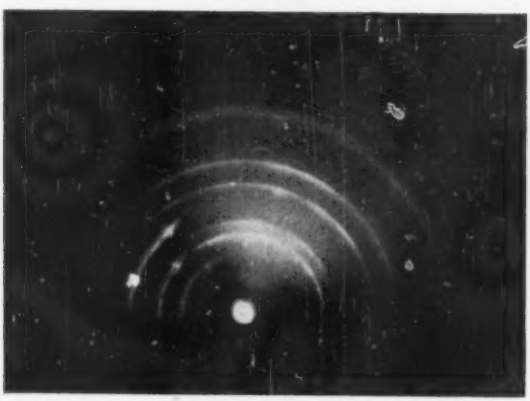

FIG. 9. Reflection electron diffraction pattern of 18-8-S stainless steel. (Specimen was polished, etched, and passivated. Arrows mark positions of diffuse bands indicative of surface oxide film.)

marked with arrows. These occur at interplanar spacings of 2.52Å., and 1.48Å. The line at 2.10Å. coincides with a line in the face-centered cubic lattice which the diffraction pattern represents.

SUMMARY

1. By the use of bromine-methanol solutions it has been possible to isolate "passive" films from electroplated chromium, ferritic stainless

steel, and austenitic stainless steel, and from the alloys "Nichrome" V and "Inconel". The films were very thin and transparent and were formed on initially film-free (pickled) surfaces by air exposure and by passivation treatments in HNO_3 and in HNO_3 containing $K_2Cr_2O_7$.

2. The passive films have been examined both by light microscopy and electron microscopy and by electron diffraction. Spectrographic analysis (qualitative) and quantitative chemical analyses of the films have been obtained. The chemical analyses of passive films from type 430 (15-16 Cr) and type 317 (18-8-S-Mo) stainless steels indicate that both chromium and iron are the primary constituents of the films. It is believed that these are present together in solid solution, probably in a spinel type of lattice.

The passive film on chromium is considered to be Cr_2O_3. The presence of other metals, copper and iron, and of silica is ascribed to contamination of the chromium oxide film.

ACKNOWLEDGMENT

The authors wish to acknowledge the assistance of J. S. Thorpe for his help in the experimental studies involved in this research, and of numerous members of the Engineering Research Laboratory for their advice and encouragement. The electron micrographs and electron diffraction patterns were taken by R. H. Fisher under the supervision of C. E. Willoughby of the Physics Section of the Chemical Department.

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APPENDIX A

Description of analytical procedures

In the chemical analysis of the oxide films reported in this paper, the procedures reported by Vernon, Wormwell, and Nurse (4) were used in making up 100-ml. solutions of a film sample. From that point the actual colorimetric procedure was somewhat modified as follows:

Iron: To 10 ml. of the solution of oxide, N/10 $KMnO_4$ was added dropwise until the solution was faintly pink. The solution was then boiled, cooled, and 5 ml. of 5% NH_4SCN in 50% acetone was added. Light of wavelength $\lambda = 4800$Å. was employed.

Nickel: To 5 ml. of solution were added:
5 ml. of 10% citric acid
5 ml. of saturated bromine water
5 ml. of 1:1 NH_4OH
2 ml. of 1% alcoholic dimethylglyoxime solution
Light of wavelength 5300Å. was employed.

Chromium: To 10 ml. of test solution, N/10 $KMnO_4$ was added until the solution was faintly pink. After boiling and cooling, 10 ml. of 1:4 concentrated H_2SO_4 was added, followed by 1 ml. of 0.25% alcoholic diphenylcarbazide. Light of wavelength 4800Å. was employed.

Silica: To 5 ml. of solution were added:
5 ml. of 5% HCl
5 ml. of 10% $(NH_4)_2MoO_4$. The solution was then allowed to stand for 1 min.
10 ml. of 17% Na_2SO_3 solution was then added and a reading was taken after 5 min.

[A blank for SiO_2 analysis consisted of the same procedure except that the $(NH_4)_2MoO_4$ was not added. The reading obtained was used as a zero setting.]

Wavelength of light employed was 6200Å.

Molybdenum: 25 ml. of sample solution

20 ml. of a solution of { 225 ml. conc. H_2SO_4 / 350 ml. conc. HNO_3 / 750 ml. H_2O }

1.5 ml. of 50% KSCN

2.5 ml. of 10% $SnCl_2$ in conc. HCl. The solution was mixed well, made up to 50 ml. and allowed to stand for 15 min. The reading was made up a wavelength of 4400Å.

Copper: 10 ml. of sample solution:

Add 5 drops 2% KNO_2

5 drops 10% acetic acid

3 ml. 5% salicylic acid in 10% alcohol.

The solution was mixed, heated in a water bath, and a reading made at a wavelength of 4400Å.

In all cases comparison blanks were run using a solution made up from a blank fusion.

THE CORROSION OF SILVER IN A WATER SATURATED CHLORINE ATMOSPHERE[1]

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ABSTRACT

The corrosion of pure silver (>99.97%) in a saturated chlorine atmosphere was studied. The corrosion rate initially indicated that above 44°C. a negative temperature coefficient was obtained. After an extended period of time the temperature coefficient was positive up to about 90°C. The effects are explained on the basis of concentration of active agent and diffusion through the film of silver chloride of the active agent.

INTRODUCTION

The purpose of this study was to observe the effect of temperature on the corrosion rate of silver in a saturated chlorine atmosphere. It is generally known that silver is more slowly acted upon by chlorine than most metals. Tamman and Koster found that (1) when chlorine acts on silver, in general "The speed of reaction varies directly with temperature, mass of the metal and concentration of the gases."

Cowper (2) found that dry chlorine gas acts very slowly on leaf or sheet silver and that light appears to have little or no effect on this reaction. Rebaul (3) found that chlorine acted more vigorously on curved silver sheet where pressure was the least and the curvature the greatest. Nowhere in the literature was found any data on the effects of a saturated chlorine atmosphere on silver for prolonged periods of time.

[1] Manuscript received June 27, 1947.

This paper prepared for delivery before the Columbus, Ohio, Meeting, April 14 to 17, 1948.

EQUIPMENT

The corrosion chambers were two pyrex desiccators installed in a constant temperature air bath capable of maintaining temperature within ± 0.5°F. (±0.28°C.). The chlorine was lead from a wet chlorine meter into the bottom of this first desiccator, which contained water to the depth of 2 inches then into the second desiccator in the same manner. The exhaust was through caustic scrubbers. The inlets and outlets of both desiccators were equipped with 3-way stopcocks. In this way there was maintained a constant supply of fresh chlorine under partial vacuum (2 inches to 3 inches 5–7.5 cm., in water) from an aspirator pump. The constant temperature air bath was equipped with a refrigeration unit in addition to heaters so that a wide range of temperatures could be maintained.

MATERIALS

The chlorine was obtained from a 100 pound commercial tank (Ohio Chemical and Manufacturing Company) holding liquid chlorine under pressure. The silver was obtained from Handy and Harman, New York, New York, and was >99.97% pure silver. This silver was double refined electrolytically before using. The cell for refining consisted of two silver cathodes and one silver anode. These were cast from 99.97% fine silver. They were immersed in pure silver nitrate containing negligible free acid, made by dissolving silver in nitric acid. A current of 30 amperes per square foot was passed through the cell. The silver crystals collected at the cathodes were recast into an anode and the process repeated. The final crystals were then washed several times in distilled water.

EXPERIMENTAL

The double refined silver was cast and rolled to between 0.010 inches to 0.015 inches. After the final rolling it was annealed at 600°C. for 15 minutes. The silver was then cut to sample size, 4.53 cm. x 2.67 cm. and a hole drilled near the top of each sample. Next the samples were pickled in 1:1 nitric acid and then thoroughly rinsed in distilled water and finally air dried. They were then weighed, put on glass hooks attached to glass racks and placed in the corrosion chambers. About 150 cc. of water were put into the bottom of each desiccator.

Before a run was started the atmosphere in the corrosion chambers was more than 96% chlorine. This was accomplished by evacuating the system by an aspirator pump and then admitting chlorine. This procedure was repeated until the desired concentration of chlorine was obtained. After the flushing cycle had been completed the rate of through-put of chlorine was adjusted so that the atmosphere in the desiccator was completely replaced once every three hours.

During the course of a run the samples were weighed several times in order that the variation in the corrosion rate could be followed. Only during the weighing periods were the samples exposed to light. It has been experimentally determined that 15 minutes exposure to normal laboratory light caused negligible weight loss due to the decomposition of silver chloride (See Table VI). It was further established that samples

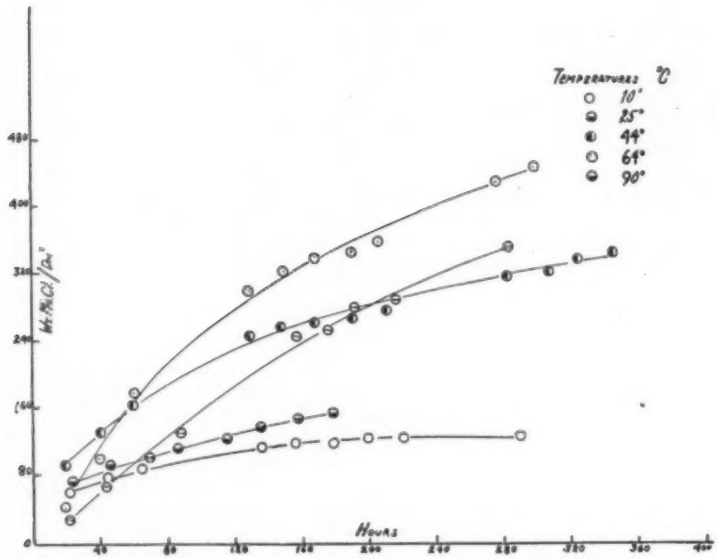

FIG. 1. Corrosion rates of silver in a saturated chlorine atmosphere at various temperature.

TABLE I.—*Average corrosion rate, mdd, gain due to AgCl formation, for individual samples*
Temperature—10°C.

Sample no.	Time, hrs.								
	0–20	22–44	44–64	64–135.5	135.5–157.0	157.0–179.0	179.0–200.5	200.5–222.0	222.0–291.5
409	86.9	19.6	25.9	14.7	2.6	0.86	2.2	3.1	0.81
410	98.4	10.9	6.8	16.5	4.4	0.95	2.4	9.7	1.9
411	81.7	19.6	15.5	9.7	6.4	1.3	1.8	1.4	2.5
412	74.7	12.5	17.3	8.4	3.9	0.95	2.2	3.9	1.1
413	83.8	14.3	15.9	11.6	3.2	1.3	3.8	3.8	0.97
414	80.8	13.1	17.2	8.5	5.7	1.4	2.9	1.9	0.93
415	32.1	29.6	32.2	6.8	4.8	3.0	2.6	3.4	1.6
416	44.8	40.2		2.8	0.0	1.4	3.7	1.4	1.6
417	99.8	3.1	10.8	2.9	6.0	1.4	4.2	3.2	0.70
418	50.3	8.8	12.3	4.3	11.7	4.5	4.6	4.2	2.0
419	42.2	1.8	11.2	2.4	2.6	1.3	0.82	3.5	1.6
420	31.3	29.2	19.3	4.7	3.8	5.8	4.6	4.7	2.0
Average gain.....	67.3	16.7	16.6	7.7	4.6	2.0	2.9	2.8	1.5
Standard deviation..	24.6	11.2	7.3	4.1	2.4	1.4	1.8	1.1	0.13
$\frac{\text{in. pen. Ag}}{\text{Yr.}}$	0.0070	0.0017	0.0017	0.0008	0.0006	0.0002	0.0003	0.0003	0.00015

exposed to chlorine continually and those weighed periodically during a run gave duplicate overall results within experimental limits.

The corrosion of silver was first recorded as gain in weight due to the formation of an adherent silver chloride film and from this the rate was calculated on the basis of mg./dm.^{2}/day. The curves (Fig. 1) were drawn where the gain in mg./dm.^{2} of chlorine is plotted against time in hours.

DISCUSSION

Over a period of time, less than 300 hours, the corrosion rate of silver in a saturated chlorine atmosphere was the least severe at 10°C. while the highest rate occurred somewhere between 64°C. and 90°C. In each case the first weighings were taken after the runs had been in progress less than 24 hours. At that point it was found that the order of increasing severity was

TABLE II.—*Average corrosion rate, mdd, gain due to AgCl formation, for individual samples*

Temperature—25°C.

Sample no.	Time, hrs.					
	0–23	23–45	45–115	115–137	137–159	159–181 5
421	72.5	18.9	22.6	7.0	7.0	6.0
422	83.5	18.7	18.6	4.3	7.0	5.5
423	66.4	15.6	12.1	4.9	3.7	1.2
424	96.9	21.8	16.4	8.5	6.4	4.2
425	86.0	24.0	15.7	9.7	6.7	4.1
426	69.6	15.6	1.7	8.5	5.5	4.5
427	69.5	21.2	3.4	8.9	6.1	5.5
428	76.9	21.2	13.2	9.9	15.0	10.6
429	76.0	22.8	20.6	19.7	16.2	12.6
430	65.3	20.8	4.2	13.9	11.1	5.5
Average gain.....	75.5	19.7	12.8	9.5	8.6	5.4
Standard deviation	9.2	2.7	6.7	4.3	3.8	3.0
in. pen. Ag ..... Yr.	0.0079	0.0021	0.0013	0.0010	0.0009	0.0008

90°C., 64°C., 10°C., 25°C. and 44°C. (Fig. 1 and Tables I–V). In this study the chlorine was saturated with water vapor so that an increase in temperature increased the water vapor pressure which in turn decreased the mole fraction of chlorine present. As the temperature increased, this would have the effect of decreasing the concentration of the corroding medium.

The solubility of chlorine in water decreases with an increase in temperature. At 100°C. the solubility of chlorine in water is zero while at 0°C., 1.46 g. of chlorine are soluble in 100 g. of water (4), both at 760 mm. pressure. As was stated earlier the rate of corrosion of silver in a dry chlorine atmosphere is considerably less than in the presence of water vapor. It is therefore probable that a liquid phase, chlorine in water solution, is the active agent in the moist atmosphere. If this were the case then an increase in temperature would decrease the concentration of the corroding medium still further due to the fact that the solubility of chlorine

in water decreases with an increase in temperature. It has been demonstrated many times that where diffusion is the controlling factor, a parabolic

TABLE III.—*Average corrosion rate, mdd, gain due to AgCl formation, for individual samples*
Temperature—44°C.

Sample no.	Time, hrs.												
	0–18	18–39	39–60	60–129.5	129.5–148.5	148.5–169.5	169.5–190.5	190.5–212.0	212.0–281.0	281.0–303.0	303.0–324.5	324.5–346.5	346.5–368.5	368.5–439.0
343	95.7	45.6	45.1	20.8	17.6	4.8	7.9	13.5	7.9	12.6	14.0	11.2	2.7	11.6
344	96.8	47.2	43.5	22.4	12.8	6.8	8.2	10.8	12.0	1.8	18.4	12.4	5.7	10.9
345	109.0	24.7	41.5	22.6	15.0	0.0	11.6	10.5	5.8	6.1	17.5	5.5	3.6	9.9
346	154.0	36.2	43.5	26.8	13.3	5.2	12.8	21.4	6.2	9.1	1.9	11.8	5.7	9.8
347	141.0	39.4	37.0	32.6	4.6	17.7	7.9	6.4	6.1	3.5	8.6	7.5	5.3	7.1
348	130.0	41.8	43.5	23.8	12.3	3.7	4.6	7.7	2.8	12.6	8.4	6.7	6.7	6.6
Average gain	123.0	39.2	42.2	24.8	12.5	6.4	8.9	11.7	6.8	7.4	13.7	9.1	5.0	9.3
Standard deviation	23.3	7.5	2.5	3.9	3.9	5.5	3.0	4.9	2.9	3.9	4.8	2.7	2.7	1.8
in. pen. Ag / Yr.	0.0120	0.0041	0.0042	0.0026	0.0013	0.0005	0.0009	0.0012	0.0007	0.0007	0.0014	0.0009	0.0005	0.0009

TABLE IV.—*Average corrosion rate, mdd, gain due to AgCl formation, for individual samples*
Temperature—64°C.

Sample no.	Time, hrs.									
	0–18.5	18.5–48.0	48.0–61.0	61.0–128.0	128.0–149.0	149.0–168.0	168.0–189.0	189.0–207.5	207.5–277.0	277.0–348.0
373	53.7	56.0	115.0	38.9	50.3	9.6		16.6	16.6	8.0
374	66.3	70.9	94.4	34.2	31.4	14.0	8.5	7.6	16.6	0.0
375	55.9	80.5	79.7	51.6	25.1	21.2		13.2	9.3	14.4
376	58.5	44.9	86.0	62.4	6.1	0.0		15.1	13.9	5.7
377	37.4	66.1	66.1	48.5	19.4	15.8	7.7		10.9	9.0
378	50.9	66.1	98.1	58.5	40.7	31.6		8.2	24.5	5.9
379	54.9	33.6	140.3	36.6	47.6	32.6			28.4	42.5
380	65.1	32.5	128.9	22.1	7.5	24.4		9.2	38.4	43.3
381	49.1	36.8	115.0	37.8	0.0	2.0	10.5	6.8	32.2	33.8
382	40.6	46.5	83.4	41.0	16.3	22.1	20.4	21.1	30.0	36.7
383	40.8	88.0	63.0	37.4	19.1	36.4	2.3	18.1		
384	38.1	100.8	34.7	27.9	35.9	41.8	12.6	18.0	26.8	26.2
Average gain	50.9	68.6	93.0	41.5	25.0	20.9	10.6	13.2	22.5	22.1
Standard deviation	9.6	22.9	28.3	11.5	15.7	11.1	11.1	4.8	8.7	17.0
in. pen. Ag / Yr.	0.0053	0.0069	0.0091	0.0043	0.0026	0.0022	0.0022	0.0013	0.0023	0.0023

relationship exists between weight gain and time. These studies have been summarized by Evans (5). Fig. 2 is a plot of the square of the weight gained versus time. With the exceptions of the line representing 10°C., the weight gained, squared, is parabolic after about 120 hours. A very

TABLE V.—*Average corrosion rate, mdd, gain due to AgCl formation, for individual samples*
Temperature—90°C.

Sample no.	Time, hrs.								
	0–21.5	21.5–43.0	43.0–64.5	64.5–85.5	85.5–155.0	155.0–171.5	171.5–193.5	193.5–215.0	215.0–285.0
397	39.4	42.5	32.6	19.7	37.1	14.5			
398	35.2	38.4	30.4	18.7	33.0	10.0	27.4	11.7	27.4
399	44.9	35.6	22.8	23.4	36.7	11.8	23.2	12.1	19.4
400	25.6	21.8	19.2	25.6	27.8	8.0	31.6	15.2	23.4
401	43.5	39.0	31.9	18.3	29.4	18.6	18.8	12.4	17.8
402	31.9	36.6	24.0	17.2	25.6	9.3	28.3	15.9	21.4
403	28.9	39.1	38.6	22.0	28.4	12.3	16.1	10.2	14.7
404	28.3	54.8	30.5	26.3	23.3	7.1	14.9	13.0	17.4
405	31.6	40.7	30.8	22.4	25.0	10.2	16.0	28.6	20.2
406	28.9	70.4	9.3	33.2	18.8	21.2	42.9	23.2	24.4
407	29.9	40.0	28.1	28.0	29.3			12.7	24.9
408	24.1	30.8	19.1	23.8	21.2	8.7	30.4	13.7	17.2
Average gain	32.6	41.5	26.6	23.2	28.0	11.9	22.4	15.3	20.5
Standard deviation	6.5	11.0	7.6	4.5	5.5	4.3	8.9	5.4	3.8
in. pen. Ag / Yr.	0.0035	0.0043	0.0028	0.0024	0.0029	0.0012	0.0023	0.0017	0.0021

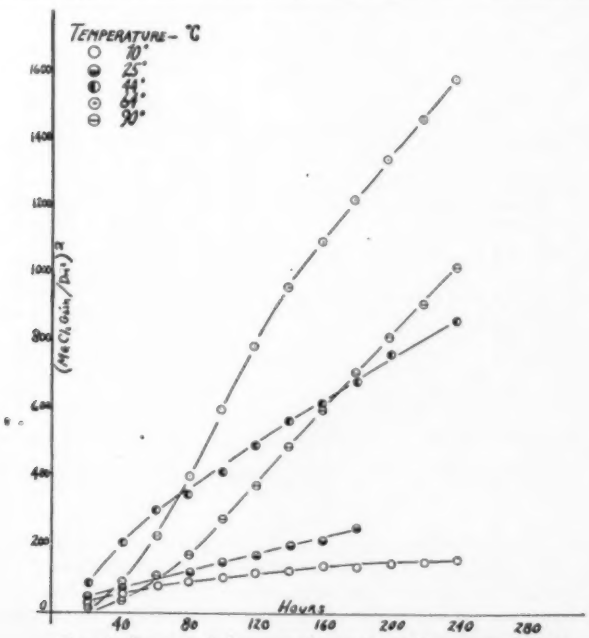

FIG. 2. Square of the corrosion rate of silver versus time

slight curvature however is maintained by the 10°C. line. It can be concluded from this that at higher temperatures, after an initial period, the factor controlling corrosion is diffusion. The film of silver chloride must be built up to a certain thickness before diffusion can control the corrosion

TABLE VI.—*Loss in weight of silver samples exposed to light, due to decomposition of silver chloride*

Sample no.	Time exposed	No. 1 weight	Time exposed	No. 2 weight	Time exposed	No. 3 weight	Time exposed	No. 4 weight	Gain or loss wt.
	Min:sec.		*Min:sec.*		*Min:sec.*		*Min:sec.*		
373	0	5.3008	6:05	5.3008	15:05	5.3008	24:45	5.3006	−0.0002
374	0	5.3298	10:45	5.3296	19:00	5.3296	29:45	5.3296	−0.0002
375	0	3.9701	8:40	3.9700	9:05	3.9700	25:10	3.9700	−0.0001
376	0	4.2050	10:55	4.2050	17:10	4.2050	1:32:25	4.2048	−0.0002
377	0	3.8220	1:03	3.8220	6:47	3.8220	1:31:33	3.8215	−0.0005
378	0	4.7380	7:45	4.7379	15:00	4.7379	24:20	4.7379	−0.0001
379	0	2.7052	12:00	2.7052	23:20	2.7052	33:50	2.7052	±0.0000
380	0	2.7163	18:30	2.7163	28:00	2.7162	35:00	2.7162	−0.0001
381	0	2.6399	20:15	2.6399	27:25	2.6400	36:25	2.6400	+0.0001
382	0	2.5197	16:35	2.5197	26:05	2.5197	36:40	2.5197	±0.0000
383	0	2.6315	16:45	2.6315	37:45	2.6314	35:20	2.6314	−0.0001
384	0	2.3895	4:15	2.3894	16:40	2.3894	23:20	2.3894	−0.0001

TABLE VII.—*Average corrosion rate, mdd, for individual samples—gain due to AgCl formation*

Sample no.	90°C.					44°C.				
	Hrs.									
	0–18.5	18.5–40	40–57	57–79	79–149–	149–170.5–	170.5–193.0	193.0–215.0	215.0–237.0	237.0–307.0
671	46.0	72.6	18.1	27.8	21.4	7.2	2.7	0.0	0.87	2.0
672	41.9	71.7	8.5	44.1	25.8	9.5	2.1	0.0	2.3	1.5
673	45.4	77.2	31.8	36.4	23.6	9.8				
674	44.5	84.9	7.5	35.6	49.2	19.1	5.1	1.8	4.5	2.8
675	37.1	90.4	5.2	8.1	34.1	7.6	3.7	0.0	2.6	2.4
676	37.8	95.5	11.2	21.2	24.6	8.7	2.9	8.1	2.1	2.6
677	56.0	17.1	6.6	21.3		9.6	5.2	1.8	7.1	5.1
678	37.6	16.6	7.5	15.6		8.6	6.1	0.0	4.4	4.0
679	45.6	18.5	17.2	22.2		7.1	3.2	1.4	6.4	4.5
680	33.0	12.7	6.8	14.5		9.9	6.9	0.0	4.9	3.2
681	44.5	29.2	34.3	24.5		11.2	8.1	0.23	8.1	5.0
682	40 0	36.4	58.3	51.8		8.3	6.1	1.4	5.0	3.7
Average gain	43.3	52.8	17.6	26.8	29.6	9.7	4.74	0.84	4.3	3.3
Standard deviation	7.8	10.8	12.1	11.6	9.5	3.0	1.9	0.54	1.9	1.1
in. pen. Ag / Yr.	0.0045	0.0054	0.0019	0.0026	0.0031	0.0010	0.00049	0.00009	0.00044	0.00034

rate (see Fig. 2). In order to establish an approximate coefficient for the diffusion of the chlorine through the silver chloride film, rates during the period of 140 to 180 hours were determined graphically (Fig. 1) at the various temperatures used. As indicated in Table VIII these rates were corrected for the thickness of the silver chloride film using as a basis, a film

TABLE VIII.—*Tabulated calculations of relative corrosion rates*

754 mm.—av. atmospheric pressure; 724 mm.—working pressure (chlorine + water)

Temp.	Measured rate	Film thickness	Correction for film thickness	N mol. fraction Cl_2 in atmos.	(R_G) correction for cons. of Cl_2 in gas	Sol. of Cl_2 in water t. & p.-	(R_L) correction for Cl_2 in liquid phase	1/T	Log. R_G	Log. R_L
°C.	*mg/dm²/ 40 hrs.*		*100 mg Cl/dm²*			*gm/L*				
10	8.0	1.16	9.3	0.988	9.4	9.60	0.98	0.00353	0.973	−0.010
25	16.0	1.47	23.6	0.968	24.4	6.43	3.67	0.00335	1.387	0.565
44	26.4	2.56	67.5	0.908	74.3	4.23	15.9	0.00315	1.871	1.201
64	40.4	3.28	131.2	0.754	174.2	2.90	45.3	0.00297	2.241	1.656
90	49.6	2.36	117.1	0.274	428.0	1.42	82.5	0.00275	2.631	1.915

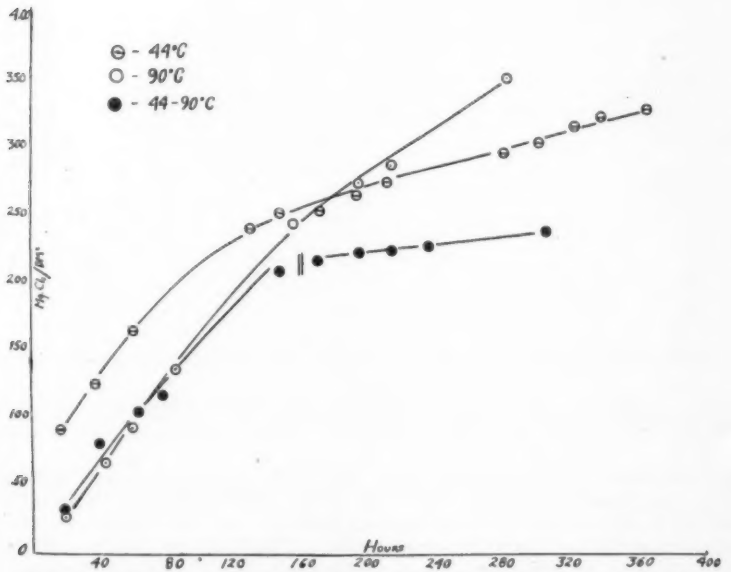

FIG. 3. The effects on the corrosion rate of a silver chloride coating applied at 44°C. and 90°C.

containing 100 mg. of chlorine as silver chloride. The next correction would apply if the reactions were between gaseous chlorine and solid silver. It consists of correcting for the mole fraction of water vapor in the atmosphere. The third correction would apply if the reaction were between an

aqueous solution of chlorine and solid silver. In order to make this correction, data for solubility of chlorine in water at various temperatures and pressures were obtained from work done by Adams and Edmonds (6). From the calculated relative rates it can be seen that a high temperature coefficient was obtained. Plots of the logarithm of the relative rates versus the reciprocal of the absolute temperature for both conditions of gas solid reaction, Fig. 4, and liquid solid reaction, Fig. 5, indicate that either the temperature coefficient was not an exponential function or the diffusivity through the film varies with the temperature at which the film is formed. If the tighter film is formed at higher temperatures, the deviation from a straight line would be in the direction that was obtained. From the

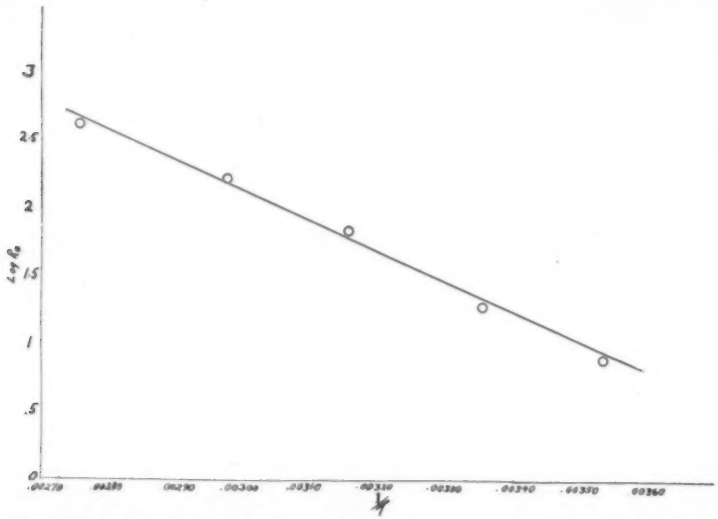

Fig. 4. Logarithm of relative corrosion rate versus the reciprocal of the absolute temperature, assuming a gas-solid reaction.

work of Mollwo (7) in which the diffusion of gaseous bromine through potassium bromide crystals was studied the diffusivities at 500°C., 600°C. and 700°C. were 2.33 x 10^{-4} cm^2/sec., 2.64 x 10^{-4} cm^2/sec., and 3.33 x 10^{-4} cm^2/sec., respectively at one atmosphere. This gave an increase of only one part in about three for a temperature rise of 200°C. The temperature coefficient from our experimental results were of an entirely different order of magnitude, $\frac{Rt + 10°C.}{Rt} = 1.6$, where R is the relative rate. Taylor (8), reports temperature coefficients of an exponential nature for liquid diffusion. He reported one system in which, for a 10°C. rise in temperature, diffusion coefficients increased by a factor of 1.48. He further reports that the magnitude of the temperature coefficient increases with a decrease in the diffusion coefficient. From the slope of the line in plot no. 5, it has been

calculated that the increase in reaction rate is by a factor of 1.8 for a 10°C. rise in temperature. The temperature coefficient is of the expected order of magnitude for liquid diffusion and therefore it is concluded that the liquid phase, chlorine in water, is involved in this corrosion mechanism.

In order to verify the postulation that as the temperature increases the character of the film formed changes in such a manner as to decrease the rate of diffusion of the active material through it, an experiment was performed as follows: the conditions used in determining the corrosion rate at 90°C. were repeated up to 149 hours at which time the temperature was lowered to 44°C. and the conditions used to determine the corrosion rate at 44°C. were continued for the remainder of the test. The results of this

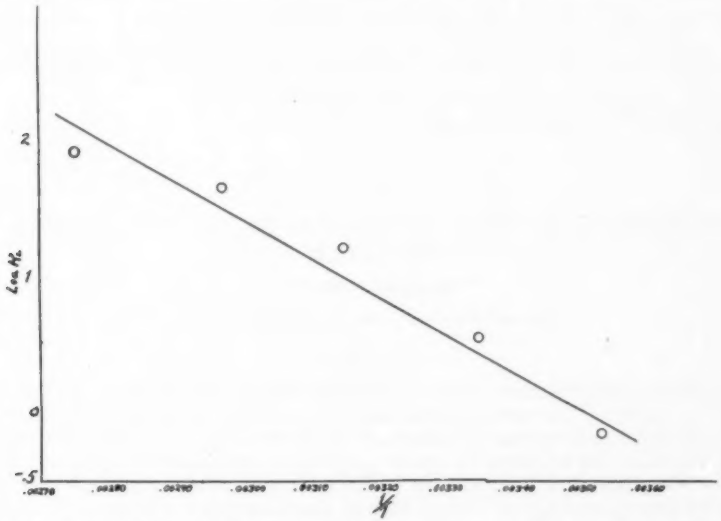

FIG. 5. Logarithm of relative corrosion rate versus the reciprocal of the absolute temperature, assuming a liquid-solid reaction

experiment are illustrated in Fig. 3 (see Table VII). It can be seen that when the film is formed at a higher temperature the rate of corrosion at a lower temperature is considerably reduced from the value that would be obtained if the lower temperature were used throughout. This verifies the deviation from the straight line in Fig. 5.

CONCLUSION

At 280 hours, the most severe corrosion occurs at 64°C. However if enough time were allowed, the corrosion curve at 90°C. might eventually cross the 64°C. curve and therefore be the most severe of the temperatures studied (see Fig. 1). The least severe corrosion rate occurred at 10°C. except for a brief period initially. In the corrosion of silver in a saturated, moist chlorine atmosphere, the active corrodant is the liquid phase, chlorine

in water, solution. The corrosion rate of silver has a positive temperature coefficient but it is necessary that enough time be allowed to establish a film of silver chloride, sufficiently thick, to make the diffusion of the chlorine to the silver surface, the controlling factor.

The authors wish to express their appreciation and gratitude to Wallace and Tiernan Inc., of Newark, New Jersey, for equipment and funds and to Mr. G. M. Booth and Mr. M. H. Cubberley of that company for their assistance and guidance.

Any discussion of this paper will appear in the discussion section of Volume 93 of the Transactions of this Society.

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INHIBITION OF STEEL CORROSION BY SODIUM NITRITE IN WATER[1]

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ABSTRACT

A study has been made of the effect of sodium nitrite on the corrosion of steel in water. The test methods included total and alternate immersion, a recirculation apparatus and potential measurements. The concentration of sodium nitrite required to *inhibit* steel corrosion depends on the conditions of motion and temperature. The inhibiting effect of sodium nitrite can be interpreted by solution potential measurements. The mechanism of inhibition is probably the formation of a protective oxide coating.

INTRODUCTION

During the past few years a number of references have been made to sodium nitrite as a corrosion inhibitor. Its main uses have been as an inhibitor in gasoline pipe lines and in antifreeze mixtures (1). This paper presents some work on sodium nitrite as an inhibitor of corrosion of steel in water.

MATERIALS USED

The steel used for all the tests was low carbon steel. The panels were bright cold-rolled steel and the tubes were Shelby seamless tubing. Before

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use the test pieces were heated at 1020°F. (549°C.) for one hour and cooled in the oven. They were then descaled in 6N HCl containing 3% Rodine

TABLE I.—*Composition of waters used in tests*

	Ottawa tap water	Toronto tap water
	p.p.m.	*p.p.m.*
Alkalinity as $CaCO_3$	19.0	90
Residue	100	180
Silica	1.6	2
Calcium	8.8	37
Magnesium	50	8
Bicarbonate	23.2	90
Sulphate	25	27
Chloride	1.0	18
Total hardness ($CaCO_3$)	46	123
pH	8.6	8.0

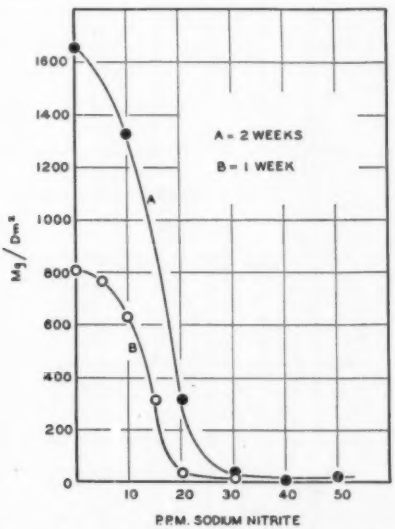

FIG. 1. Corrosion losses of steel panels in mg./dm² showing the inhibiting effect of sodium nitrite in Ottawa tap water in a rocker test. The two week run requires a higher concentration of nitrite for complete inhibition, probably due to the breakdown of inhibitor.

as inhibitor, washed in water and methyl alcohol and dried. After test they were again pickled, washed, dried and weighed.

The principal water used was Ottawa tap water, the analysis of which is given in Table I.

METHODS OF TEST

The methods of testing were similar to those used in a previously de-

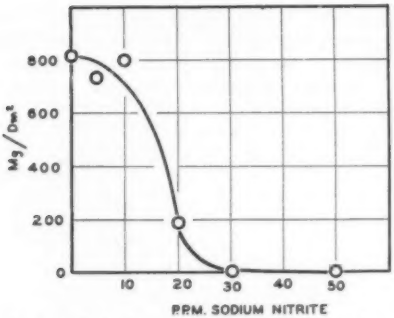

FIG. 2. Corrosion losses of steel panels in mg./dm² showing the inhibiting effect of sodium nitrite in Toronto tap water. Duration of tests—7 days.

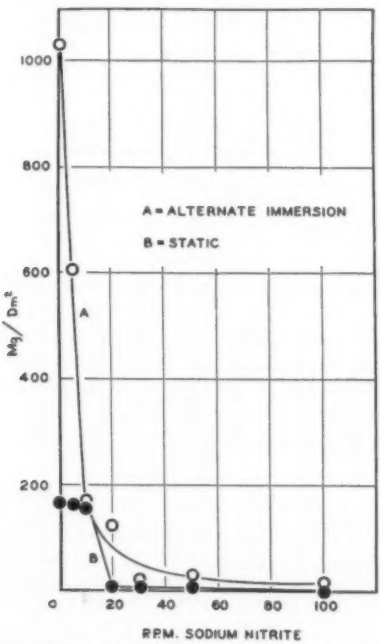

FIG. 3. Showing the effect of alternate immersion and static immersion on the inhibiting concentrations of sodium nitrite in Ottawa tap water. A higher concentration is required in static immersion. Duration of tests—7 days.

scribed study of sodium hexametaphosphate (2). In addition some e.m.f. measurements have been made and compared with the corrosion results. In all cases p.p.m. refers to $NaNO_2$.

A. Rocker immersion

This apparatus has been described previously (3). Steel panels, 4 in. x 1 in. (10 cm. x 2.5 cm.) were used. The temperature was 90°F. (32°C.) and the flow equivalent to 1400 cc./min. Runs were made with Ottawa tap water and Toronto tap water. Corrosion was measured by weight loss. In Fig. 1 is shown two curves obtained by one week and two week runs. In Fig. 2 is a curve obtained with Toronto tap water for comparison.

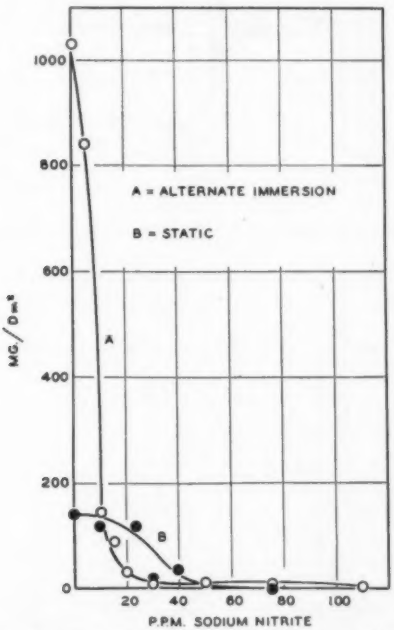

FIG. 4. Same as Fig. 3 but using Toronto tap water

B. Alternate immersion

This test consisted of dipping the 4″ x 1″ panels in and out of 750 cc. of solution 14 times per minute. The panels were always wet. The temperature was 90°F. (32°C.). In Fig. 3 is shown a curve obtained with Ottawa tap water and in Fig. 4 curves obtained with Toronto tap water. In both cases comparisons with static immersion are given. It should be noted that inhibition is obtained with both static and moving conditions, although the concentration required under static conditions is higher.

C. Circulation

In this test, the solution is recirculated through steel tubes of varying diameters in series, insulated from one another by rubber and glass, with one tube not in line acting as a dead end. The volume of the thermostatted

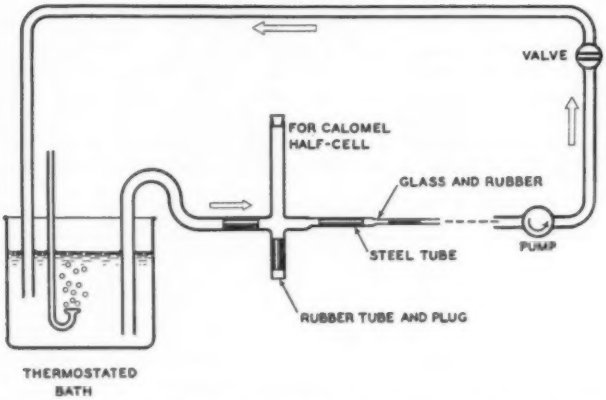

FIG. 5. Circulation apparatus. The water passes through the tubes

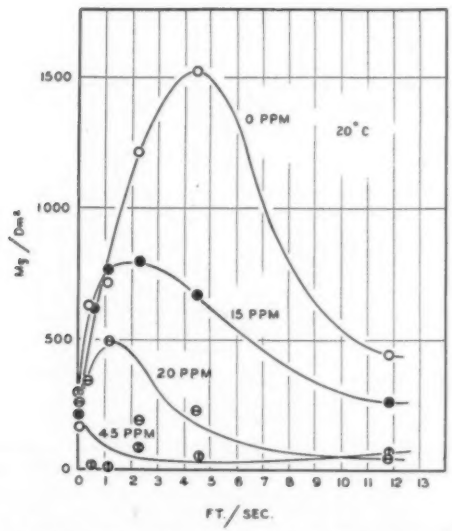

FIG. 6. Effect of rate of flow of solution over steel on corrosion. Curves show effect of concentration of inhibitor. The rate of flow at which maximum weight loss occus decreases with increasing concentration. Duration of tests—5 days. Temperature—20°C.

bath was 28 liters, and 8 liters of solution are replaced daily. In most of the tests, air was bubbled through the solutions to ensure saturation. Fig. 5 is a diagrammatic sketch of the apparatus.

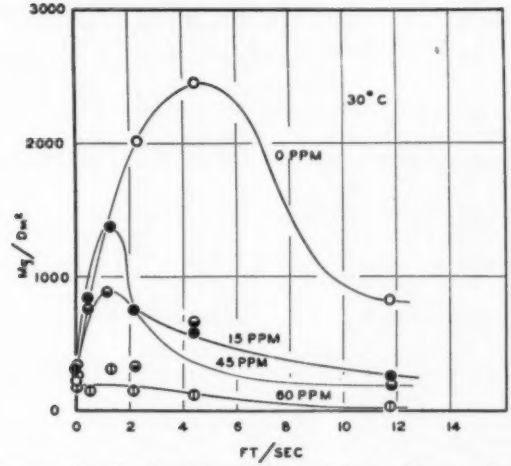

FIG. 7. Same as Fig. 6. Duration of tests—5 days. Temperature—30°C

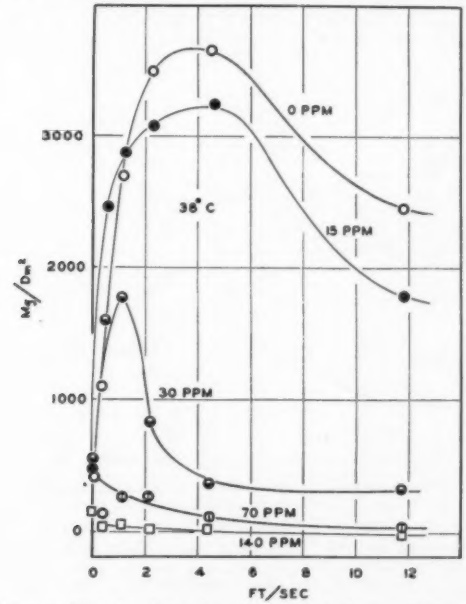

FIG. 8. Same as Fig. 6. Duration of tests—7 days. Temperature—38°C

D. Static

As has been pointed out above, sodium nitrite inhibits corrosion in static solution at about 30 p.p.m. Any increase in concentration above this value up to at least 10,000 p.p.m. has no further effect.

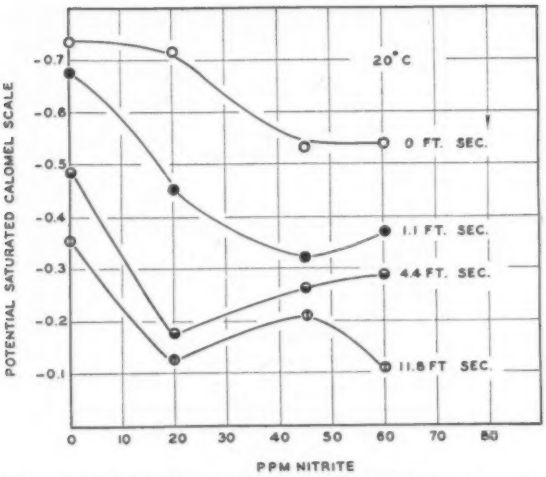

FIG. 9. Shows relationship of potential of steel to inhibitor concentration at various rates of flow. Time—5th day. Temperature—20°C.

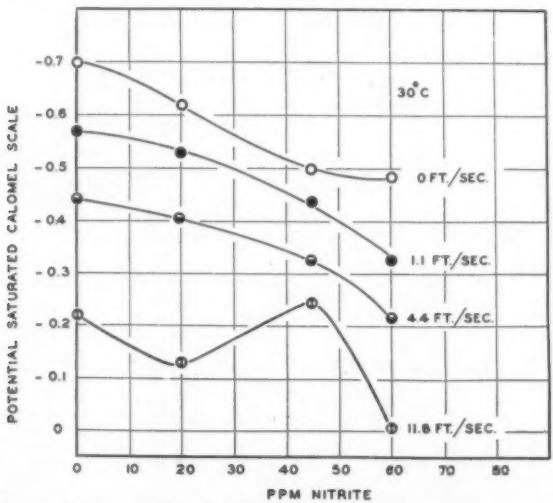

FIG. 10. Same as Fig. 9. Time—5th day. Temperature—30°C

E. E.m.f. measurements

In conjunction with the circulation tests, e.m.f. measurements of the various tubes both against each other and compared to a Calomel Half-cell were made. These are summarized in Fig. 9, 10 and 11. Fig. 12 is a replot of Fig. 10 to show the effect of speed on voltage. As well as these measure-

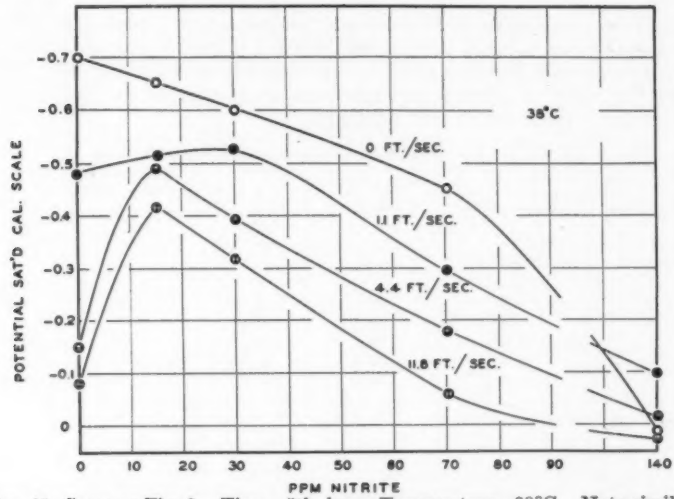

FIG. 11. Same as Fig. 9. Time—5th day. Temperature—38°C. Note similarity between some of p.p.m.—potential curves to rate of flow—weight loss curves.

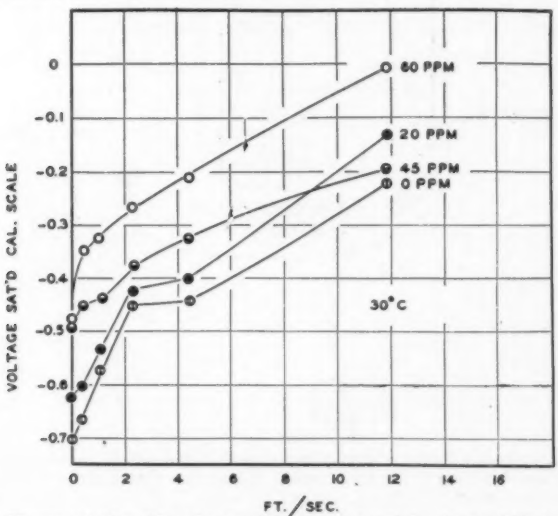

FIG. 12. Shows relationship of rate of flow to potential. Note shift to passive potentials with both increasing concentration and rate of flow. Time—5th day. Temperature—30°C.

ments, some current measurements were made by short circuiting tubes through a microammeter and current and voltage measurements made simultaneously. These measurements are shown in Table II.

E.m.f. measurements were also made using an apparatus shown in Fig. 13. The metal piece was set in the plastic using a metallographic mounting. A few typical runs showing e.m.f. versus time are shown in Fig. 14. Fig. 15 shows the effect of stirring and interruption of stirring on the voltage of steel in water obtained in this apparatus.

TABLE II.—*Reynolds numbers for various velocities and temperatures*

Tube number	Diameter of tube	Velocity	Reynolds number		
			20°C.	30°C.	38°C.
cm./sec.	*centimeters*	*cm./sec.*			
1	2.48	0	0	0	0
2	2.48	12.8	3,160	3,950	4,650
3	1.59	34.5	5,450	6,800	8,010
4	1.11	68.6	7,570	9,460	11,100
5	0.79	135.0	10,600	13,300	15,600
6	0.48	360.0	17,200	21,500	25,300

Rate of flow—4 liters per minute

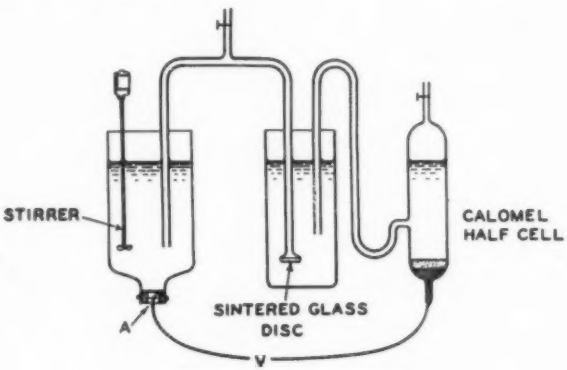

FIG. 13. Apparatus used for measuring potentials of small pieces of metal set in plastic. Sintered glass disc used to prevent diffusion. The sample can be ground or polished in the plastic button.

In connection with the inhibition studies, measurements of the breakdown of sodium nitrite in the presence and absence of steel have been made (4). These are not as yet complete and will be published at a later date. However, the indications are that sodium nitrite by itself is quite stable in solution up to 60°C., but that in the presence of corroding steel, it begins to decompose, its rate of decomposition depending on the rate of corrosion of the steel, and the temperature (4).

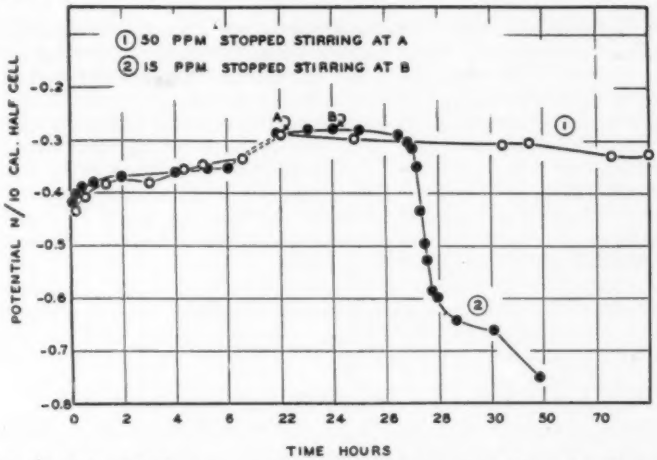

FIG. 14. Potential time curves for steel in two concentrations of sodium nitrite. These show the effect of stirring on the voltage with both sufficient and insufficient inhibitor. Note the time lag for the breakdown of the passive potential on Curve 2. Temperature—23° C.

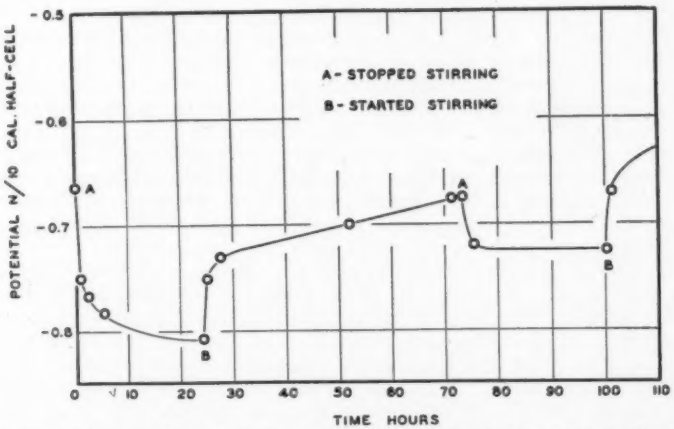

FIG. 15. This shows the effect of intermittent stirring on the potential of steel in water. The start of the experiment is at the start of rusting of the steel. The rate of diffusion determines the time required for setting up steady potentials.

Some X-ray diffraction studies have been made on steel specimens on which corrosion has been completely inhibited by sodium nitrite. These show only iron oxides.

GENERAL OBSERVATIONS

In general, as the concentration of sodium nitrite was increased, the

attack changed from overall attack to partial attack and pitting, and then to complete protection. In some cases, the panels actually showed a slight gain in weight, where there was complete inhibition and no after pickling. There was some evidence of interference color film formation.

The oxygen concentration of all the solutions in all the tests was near saturation with respect to air. This was ensured in the circulation tests by bubbling air into the baths. Previous tests had shown that both the rocker and alternate immersion machines gave saturated solutions.

The pH of all the solutions after test was of the order of 7.6. No attempt was made to adjust the pH. Sodium nitrite in the concentrations used has little effect on the pH of Ottawa tap water.

The voltage measurements were made with a Rubicon Portable Potentiometer using an outside galvanometer. Sufficient resistance was inserted in the circuit during nonbalance to reduce current, and thus polarization, to a minimum.

DISCUSSION

All the temperatures are below the range at which a depletion of oxygen, due to the lowering of solubility of oxygen in water at higher temperatures, had a marked effect. That is, the corrosion in all cases increased with temperature and a greater amount of nitrite was required to give inhibition. Both these facts can be seen by a comparison of Figs. 6, 7 and 8.

The availability of oxygen (and sodium nitrite) to the metal surface is not only dependent on the concentration but also on the type of test. Thus, although the rocker and alternate immersion test solutions were saturated with air, the draining effect of the alternate immersion probably gave a higher availability of the oxygen and nitrite to the surface by decreasing the thickness of the diffusion layer. This explains the sharp drop in corrosion in the alternate immersion test. Also in the circulation tests, the higher speeds, with their subsequent higher turbulence gave greater availability of both oxygen and nitrite. Table II shows the relationship between Reynold's numbers and the speeds used. Water changes from streamline to turbulent flow at a Reynold's number of about 2100. Consequently, all the flow rates in the circulation tests gave turbulent flow.

The inhibiting action of sodium nitrite is probably due to the formation of a tight iron oxide film caused by a reaction between the metal and sodium nitrite. This reaction between iron and nitrite acting as an oxidizing agent is borne out by several of the observations. Thus the speed of circulation at which the maximum corrosion occurred decreased with increasing sodium nitrite. This can be explained if we assume that oxygen of high enough availability, (high replacement at the metal surface), can act as an inhibitor. This is shown to be true by Evans' and Mears' (5) drop experiments and by the shape of our curves, that is, corrosion increases with speed and falls off with a further increase in speed. In the drop experiments the probability of attack decreased with increasing oxygen concentration. The indication is that sodium nitrite decomposes appreciably only in the presence of iron and that iron must be corroding. In other words, bare anodic areas must exist for this decomposition. (Note the convergence of the two week and one week curves shown in Fig. 1.).

In addition, voltage measurements indicate an oxide layer with inhibition

(voltage −0.3 static solutions) and a breakdown of the oxide layer without inhibition (voltage −0.7 when rusting in static solutions). This oxide layer is somewhat stable, as indicated by the two hour lag in the breakdown of the potential when stirring of the 15 p.p.m. sodium nitrite solution was stopped (Fig. 14). Time is also required to build up a stable protective layer, as is shown by the gradual rise of the potential at the beginning of the 50 p.p.m. nitrite experiment (Fig. 14). This time requirement also was evident in the daily voltage measurements of the tubes in the circulation apparatus. The time voltage curves at inhibiting concentrations are quite similar to those which are obtained using stainless steel (6).

The similarity of some of the concentration versus voltage runs at 38°C. to the rate of flow versus weight loss runs indicated that at least at certain speeds and temperatures it was the combined effect of nitrite and oxygen

TABLE III.—*Effect of sodium nitrate on solution potentials and current flow between steel tubes in circulation test at 30°C.*

Anode		Cathode		Current microamperes	Anode potential against saturated calomel half-cell-volts	
Tube no.	Velocity	Tube no.	Velocity		Water	60 p.p.m. $NaNO_2$
	cm./sec.		*cm./sec.*			
1	0			open circuit	−0.726	−0.487
2	12.8			open circuit	−0.698	−0.358
3	34.5			open circuit	−0.670	−0.375
4	68.6			open circuit	−0.546	−0.330
1	0	2	12.8	1.25	−0.715	−0.420*
1	0	2	12.8	8.3		
3	34.5	4	68.6	1.9	−0.668†	

*Potential of cathode −0.419.

† Potential difference between tubes <0.1 mv.

The closed circuit measurements were made by short circuiting the tubes through a microammeter. The potentials returned to the original values when the circuits were opened. Note that the tube with the higher velocity was cathodic in all cases.

which gave inhibition. This again showed the relationship between voltage and tendency toward corrosion.

The rate of flow of the solution affects the voltage of the steel by reducing the thickness of the diffusion layer and making the constituents of the solution more available to the metal surface. In effect, the higher rates of flow are supplying both more oxygen and nitrite. At partial inhibition, there is an uneven distribution of anodic and cathodic areas with resultant pitting. In this pitting range there is some overlapping in both weight losses and voltage at the various concentrations and rates of flow. The voltage exhibited by a piece of steel in a solution is made up of an average of the polarized voltages of the various areas on that piece of steel (7). Thus, as we go from overall corrosion to complete protection by varying the concentration of nitrite and the rate of flow, there is a tendency for the voltage to change from that of corroding metal to passive metal, but because of the localized nature of the corrosion (pitting) this voltage does not vary regularly with concentration. This accounts for the irregularities

shown in Fig. 12. It should be kept in mind that the actual value of the potential in all these cases must be considered together with the rate of flow of the solution and the temperature if it is to be considered as a corroding or passive potential. Thus a potential of -0.3 in a static solution indicates passivity, but does not indicate passivity when the relative flow between metal and solution is 11.8 ft./sec. In a system where there is electrical contact between steel tubes with varying rates of flow, there is a definite tendency for current to flow and this tendency is a continuous one (see Table III). The effect of this on corrosion at inhibiting concentrations will have to be studied more fully.

The presence of a corrosion layer on the steel retarded the rate of attainment of a steady voltage when the conditions of motion were changed. This was noted particularly in the experiments with water in the apparatus shown in Fig. 13. This corrosion layer, when present as overall corrosion, also decreased the rate of corrosion with time.

The breakdown of sodium nitrite is a factor which would have to be considered in any recirculating system and would require periodic replenishment of sodium nitrite. The amount required would depend on the original concentration. This fact has been observed with sodium dichromate, where it was found that the consumption of chromate "decreases as the concentration of the chromate is increased" (8). The action of chromate is very similar to the action of nitrite and probably an oxidizing action is also involved. This is borne out by the presence of lower oxides of chromium after contact with steel. The sodium nitrite is probably broken down to nitrogen or nitrogen-hydrogen compounds. Sodium nitrate does not act as an inhibitor, a fact which is probably related to the greater stability of the nitrate radical.

Sodium nitrite acts as an anodic inhibitor. As such it is subject to the weaknesses of all anodic inhibitors in that it may stimulate pitting at concentrations below those required for complete protection. Also the fact that it is an oxygen donor may cause it to stimulate corrosion under some conditions at very low concentrations. This could account for some of the overlapping of the curves at the lower concentrations.

CONCLUSIONS

1. Sodium nitrite is an inhibitor for corrosion of steel in water under both static and motion conditions.
2. The concentration required for inhibition is less in moving solutions than in static solutions. Thus at 25°C., and with a large volume of solution compared to metal, 15 p.p.m. sodium nitrite inhibited corrosion with stirring, but did not inhibit without stirring. 50 p.p.m. sodium nitrite inhibited with and without stirring.
3. The concentration required for inhibition increases with temperature.
4. The inhibiting effect of sodium nitrite can be followed and interpreted by voltage measurements.
5. The mechanism of inhibition is probably the formation of a tight oxide layer which is formed by the combined action of nitrite and oxygen and is repaired by the nitrite.

Any discussion of this paper will appear in the discussion section of Volume 93 of the Transactions of this Society.

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